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**Impedance and Lithium-7 NMR Studies of Polymer Electrolytes
Based on Poly(vinylidene Fluoride)**

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IMPEDANCE AND LITHIUM-7 NMR STUDIES OF POLYMER ELECTROLYTES BASED ON POLY(VINYLDENE FLUORIDE)

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ABSTRACT

Composite polymer electrolytes consisting of at least 35 mol% poly(vinylidene fluoride) (PVdF) and mixtures of propylene carbonate (PC) and dimethyl formate (DMF), lithium salts (LiAsF_6 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, or $\text{LiC}(\text{CF}_3\text{SO}_2)_3$), and small amounts (~ 5 mol%) of plasticizer, either diethylphthalate (DEP) or dibutylphthalate (DBP), were investigated by differential scanning calorimetry, complex impedance analysis and ^7Li NMR spectroscopy. Despite the composite nature of these materials, they all exhibit a single glass transition temperature (T_g). Significant variations of T_g with the two different plasticizers were noted. The sample containing the $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ salt has the highest electrical conductivity of the series, $\sim 3 \times 10^{-4} \text{ S/cm}$ at 25°C . Time-dependent impedance measurements utilizing cells with lithium electrodes revealed the growth of a passivating interface layer comparable to those observed with other polymer electrolytes. The onset of NMR motional line-narrowing is correlated with T_g for all samples prepared with DBP, as is known to occur in "single component" polyether-based electrolytes. However the onset of narrowing for the samples containing DEP occurs about 30 K above T_g . Lithium-7 spin-lattice relaxation measurements exhibit non-exponential recovery profiles below T_g , with about $\sim 15\%$ of the Li species relax differently than the majority. Activation energies extracted from ^7Li T_1 data show that localized Li motion is significantly impeded in the DEP-containing samples, relative to those prepared with DBP.

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INTRODUCTION

The development of new polymeric electrolytes has played a crucial role in recent advances in secondary lithium or lithium-ion batteries.[1] In many practical battery applications solvent-free polymer electrolytes, such as poly(ethylene oxide) - lithium salt complexes, have been supplanted by highly conductive composite electrolytes containing solvents, plasticizers and other additives. For example, electrolytes based on poly(acrylonitrile) (PAN) [2] and poly(methylmethacrylate) (PMMA) [3] have been widely reported.

These gel electrolytes are formed by immobilizing liquid electrolytes (lithium salts dissolved in, for example, propylene carbonate (PC) or a mixture of PC and ethylene carbonate (EC)) in a rigid polymeric matrix. The ion transport mechanism in these composite materials appears to be dominated by the liquid electrolyte, based on the observation that the conductivity of the gel is not much lower than that of the liquid electrolyte

However recent NMR results on both PAN- [4] and PMMA-based gels [5] suggest that ionic motion is impeded somewhat by the host polymer, although the specific nature of the ion-polymer interaction remains unknown. Moreover, the gels appear to be homogeneous in that they are usually characterized by a single glass transition, rather than multiple transitions often observed in composite materials. One of the host polymers recently exploited in the successful development of Li ion battery technology is poly(vinylidene difluoride) (PVdF) [6-9]. We report electrical conductivity and ^7Li wide-line NMR measurements on several PVdF-based polymer electrolytes. Also included are data which provides information on electrochemical stability against lithium metal.

EXPERIMENTAL

Polymer electrolytes were prepared by combining PVdF (Polysciences, avg. m.w. 350,000), electrolyte solvent, consisting of a mixture of PC (Burdick Jackson) and dimethyl formamide (DMF, Aldrich), and a lithium salt, either LiAsF_6 (Lithco), $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (3M), or $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ (Covalent Associates, Inc.). To improve mechanical properties, quantities of plasticizers, either diethylphthalate (DEP) or dibutylphthalate (DBP) (both plasticizers from Fluka), were added to the mix. All reagents were High Purity Grade. Two methods of sample preparation were employed. In the first process, the PVdF was thoroughly mixed with the plasticizer followed by the addition

of a small amount of PC. The mixture was then heated to 110°C while stirring, and the rest of the PC and DMF was added. Finally the salt was added along with a small amount of THF (Aldrich), the latter to reduce the viscosity of the mixture, and the stirring was maintained until the mixture took on a homogeneous appearance. The mixture was then poured onto a glass plate, cooled to 45° and dried in a vacuum oven for 24 hours (at 45°C), resulting in free standing films. The modest drying procedure was intended to remove only the THF, but small quantities of some of the other solvents could also have been removed. The nominal sample compositions are listed in Table 1. A second procedure was employed, whereby all ingredients but the PVdF were dissolved in THF and heated to 100°C. The PVdF was then added and stirred until the viscous solution became transparent. The complex was then poured onto a glass plate and dried as in the first method. All sample manipulations were performed in either an argon or nitrogen drybox. For NMR measurements samples were sealed in 5mm OD X 23mm long pyrex tubes.

For initial characterization of the samples, differential scanning calorimetry (DSC) measurements were performed on either a Mettler TA 3000 DSC System or a TA Instruments 2910 DSC, with a typical heating rate of 10K/min and a sample mass of 5 to 10 mg. Electrical conductivity measurements were performed by complex impedance techniques with an EG&G PAR model 398 impedance system, over a frequency range of 10 to 10⁵ Hz. Stainless steel (#316) blocking electrodes were employed for the conductivity measurements, while a lithium/polymer electrolyte/lithium arrangement was implemented for passivation studies, to be described later. Variable temperature ⁷Li NMR measurements were performed on a Chemagnetics CMX-300 spectrometer, at a Larmor frequency of 116 MHz. Spectral line shapes were obtained by single-pulse excitation (typical pulse width of 2.5 μs) and spin-lattice relaxation times were determined by either inversion recovery or progressive saturation. For the sample volumes employed (1 cm³ or more), signal-to-noise ratios of 20 or greater (the lower limit corresponding to broad spectra at lower temperatures) were obtainable by averaging 50 - 100 transients. In order to assess heteronuclear dipolar contributions to the line width (reported as full-width at half-maximum), both ¹H and ¹⁹F decoupling were employed, with typically 150 W of pulsed decoupling power.

RESULTS AND DISCUSSION

The most prominent thermal features observed for all the samples are their single and strong glass transitions, typical of highly plasticized polymers. The glass transition temperatures (T_g) are listed in Table 2. Several factors can affect the T_g value, particularly the polymer/solvent ratio, and the nature of the plasticizing solvent. At fixed polymer/solvent/salt composition, in some cases the particular salt (i.e. the anion) can also influence T_g , as is well known for the plasticizing imide and methide anions. From the results in Table 2, it can be concluded that the relatively small amount of plasticizer added to improve mechanical properties (DEP or DBP) plays a major role in lowering T_g , more so than changing the salt anion. Clearly, DBP is more effective in this regard than DEP.

Arrhenius plots of ionic conductivity of three of the samples listed in Table 1, all having the same composition (including the plasticizer) except for the salt anion, are shown in Fig.1. The sample containing the methide salt (F) is over an order of magnitude more conductive than those with the imide or hexafluoroarsenate salts. Because of the relatively small difference between the T_g values among the samples containing DBP, the enhanced conductivity of sample F is partly attributed to a greater degree of cation-anion association in the methide salt. An equally important (as ionic conductivity) property of polymer electrolytes for lithium batteries is the stability of the Li/electrolyte interface, information about which can be obtained from time-dependent changes in impedance spectra. Several impedance spectra were gathered for a cell with sample A sandwiched between lithium electrodes. In the Cole-Cole representation of the data, typically three semicircular dispersions are present. Several sets of data taken at different times (corresponding to different degrees of passivation) are superimposed in Fig. 2. Analysis of the data shows that the relaxations giving rise to these dispersions are centered roughly at 10^4 , 10^2 and 10^{-2} Hz. These relaxations have been previously assigned in other polymer electrolyte systems, respectively, to the bulk conductivity of the electrolyte and the passivation layer resistance: the third relaxation is attributed to very low frequency (< 0.1 Hz) concentration gradient-driven diffusion of Li^+ ions through the thin ($\sim 100 \mu\text{m}$) layer adjacent to the Li anode.[9] The electrical resistances associated with the above three processes are plotted as a function of time in Fig. 3. The increase in R_{film} provides evidence of the growth of the passivation layer with time. The increase in R_{bulk} is less well understood, but has been observed previously in other polymer electrolytes in contact with lithium electrodes.[10]

A typical ^7Li NMR low temperature absorption spectrum is shown in Fig.4, corresponding to PVdF1 at $^\circ\text{C}$. As observed in other Li-polymer electrolytes below T_g , the spectra are characterized

by a broad main absorption, corresponding to the central $\pm 1/2$ transition, superimposed on a broader baseline which corresponds to a distribution of $\pm 3/2 \rightarrow \pm 1/2$ satellite transitions.[5] Proton decoupling experiments demonstrate that up to $\sim 75\%$ of the sub- T_g line width is attributable to heteronuclear dipolar coupling between ^7Li and protons. This effect has been reported in solvent-free polyether-salt complexes, where the protons reside on the polyether chains. [12] and in composite gel electrolytes, where the protons which give the main broadening contribution are contained in the solvating molecules (i.e. PC). [5] Polymer segmental motion above T_g results in modulation of the ^7Li - ^1H magnetic dipole interaction, which then leads to narrowing of the central transition. This effect has been documented widely in polyethers and, more recently in composite gels where, in the latter, the nature of the large-scale molecular motion is almost certainly more complicated than in the former. That is, precisely which molecular modes of freedom become activated above T_g in the composite material (e.g., solvent molecules, PVdF chain, etc.) is difficult to ascertain. [4]

Arrhenius plots of line width for the six samples in Table 1 are displayed in Fig.5. It is of interest first to note that all three samples containing LiAsF_6 have a low temperature line width that exceeds that of the other samples by about 10%. This excess line width arises from ^7Li - ^{19}F dipolar interactions, as verified by ^{19}F decoupling. At $\sim -100^\circ\text{C}$, well below T_g , the samples with LiAsF_6 exhibit approximately 15% reduction in line width upon ^{19}F decoupling, while the samples containing the other Li salts show only about a 5% decrease. Thus, there is direct evidence for cation-anion proximity in the LiAsF_6 - containing samples. Similar results have been reported for polyethers containing LiBF_4 . [13,14] The residual $\sim 5\%$ contribution is then attributed to the weaker coupling or greater distance between the Li^+ cations and fluorine atoms in the PVdF chain. In polyether - salt complexes and in gels the onset of motional line narrowing is nearly always at, or just above, T_g . [4,5,12,14] Comparison of results of Fig.5 with T_g values in Table 2 indicates that, for the most part, the PVdF samples follow this behavior. However both samples A and B, which differ from the rest in that they contain the DEP plasticizer, do not exhibit narrowing until the temperature is raised some 30 - 35K above T_g . To the best of the authors' knowledge, this anomalous result for samples A and B (i.e. the apparent decoupling of T_g and the onset of line narrowing) has not been reported previously for Li polymer electrolytes. It is noteworthy that sample C, containing the same salt as A and B but different plasticizer (DBP), has about the same rigid line width limit as A, B, but a much lower temperature onset of narrowing. That both samples

A and B exhibit nearly identical line widths indicates that both preparation methods yield essentially the same material. Likewise samples D and E, with different preparation routes but identical compositions, yield almost indistinguishable NMR line widths.

Spin-lattice relaxation recovery profiles below T_g were observed to be slightly non-exponential, with about 15% of the total ^7Li signal relaxing somewhat more slowly (by a factor of 2-3) than the rest. This result is not surprising in view of the heterogeneity of Li environments expected to exist in the composite electrolytes. Arrhenius plots of T_1 (excluding the above-mentioned non-exponential part) for the six samples in Table 1 are displayed in Fig.6. As observed in the line width results, the two methods of preparation yield essentially the same T_1 results (comparing results for A and B, and for D and E). With the exception of the methide sample (F), which also has the lowest T_g , none of the samples show clear T_1 minima, which apparently lie somewhat above the highest temperature probed (70°C). A broad T_1 minimum for sample F occurs at $\sim 50^\circ\text{C}$. Another polymer electrolyte system which exhibits T_1 minima (at the same NMR frequency as in the present study) only at relatively high temperature ($\geq 120^\circ\text{C}$) is poly(propylene oxide) complexed with Li salts,[15] while solvent-swollen gel electrolytes typically show lower temperature (~ -20 to $+15^\circ\text{C}$) T_1 minima.[5]

It is customary to extract activation energies from the high temperature side of the T_1 minimum. However because of the absence of such data, activation energies have been calculated from the approximately linear region of the available lower temperature data in Fig.6, and the results are listed in Table 2. As is usually observed for polymer electrolytes, the T_1 activation energies are considerably smaller (by an order of magnitude) than those calculated for conductivity from Fig.1 via an Arrhenius equation. This is not surprising because of the vastly different time scales probed by conductivity and T_1 measurements. That is, T_1 is sensitive to short-range, high frequency motions. Moreover, the temperature region for which the T_1 activation energies have been calculated does not overlap very much with that of the conductivity data. Nevertheless, it is dramatically evident that samples containing the DEP plasticizer exhibit a substantially higher barrier to localized lithium motion than the other samples, which all have nearly the same activation energies. Thus, as for the DSC and line width results, the changing the plasticizer has a far greater effect than changing the salt anion.

CONCLUSIONS

Several lithium polymer electrolytes based on PVdF, also containing solvents (PC, DMF) and plasticizers have been prepared by two different solvent-casting techniques, with little or no difference observed in properties with the same nominal composition. Time-dependent complex impedance analysis indicates that passivation reactions with the Li electrode occur to roughly the same extent as observed with other polymer electrolytes. The sample containing the methide salt exhibits electrical conductivity far superior to those containing the other salts, while the use of DBP as a plasticizer yields a lower T_g material than the samples made with DEP. The samples containing DEP are also characterized by somewhat anomalous ^7Li NMR results: (i) motional narrowing which does not begin until $\sim 30\text{K}$ above T_g (where T_g is already about 15 K higher than the DBP-containing material); (ii) significantly higher activation energy for short-range Li motion, as probed by T_1 . Although the NMR and DSC results suggest that the proper choice of plasticizer is crucial to Li^+ mobility, the ionic conductivity results seem to suggest that the proper choice of salt is more important.

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Table 1

Sample	% Molar Composition
A	PVDF 36.3/PC 35.8/DMF 18.5/DEP 6.1/LiAsF ₆ 3.3 (Method 1)
B	PVDF 36.3/PC 35.8/DMF 18.5/DEP 6.1/LiAsF ₆ 3.3 (Method 2)
C	PVDF 36.7/PC 36.23/DMF 18.77/DBP 4.925/LiAsF ₆ 3.375 (Method 2)
D	PVDF 36.7/PC 36.23/DMF 18.77/DBP 4.925/Imide 3.375 (Method 1)
E	PVDF 36.7/PC 36.23/DMF 18.77/DBP 4.925/Imide 3.375 (Method 2)
F	PVDF 36.7/PC 36.23/DMF 18.77/DBP 4.925/Methide 3.375 (Method 2)

Table 2

Sample	T _g Values (°C)	T _i Activation Energies
A	-60.0	0.195
B	-57.5	0.211
C	-72.5	0.128
D	-76.0	0.120
E	-76.1	0.128
F	-83.1	0.133

FIGURE CAPTIONS

Figure 1. Arrhenius plots of electrical conductivity for samples A (squares), C (circles) and F (triangles) (Table 1).

Figure 2. Representative Cole-Cole impedance plots at several different times. The cell consisted of sample A (Table 1) between Li electrodes.

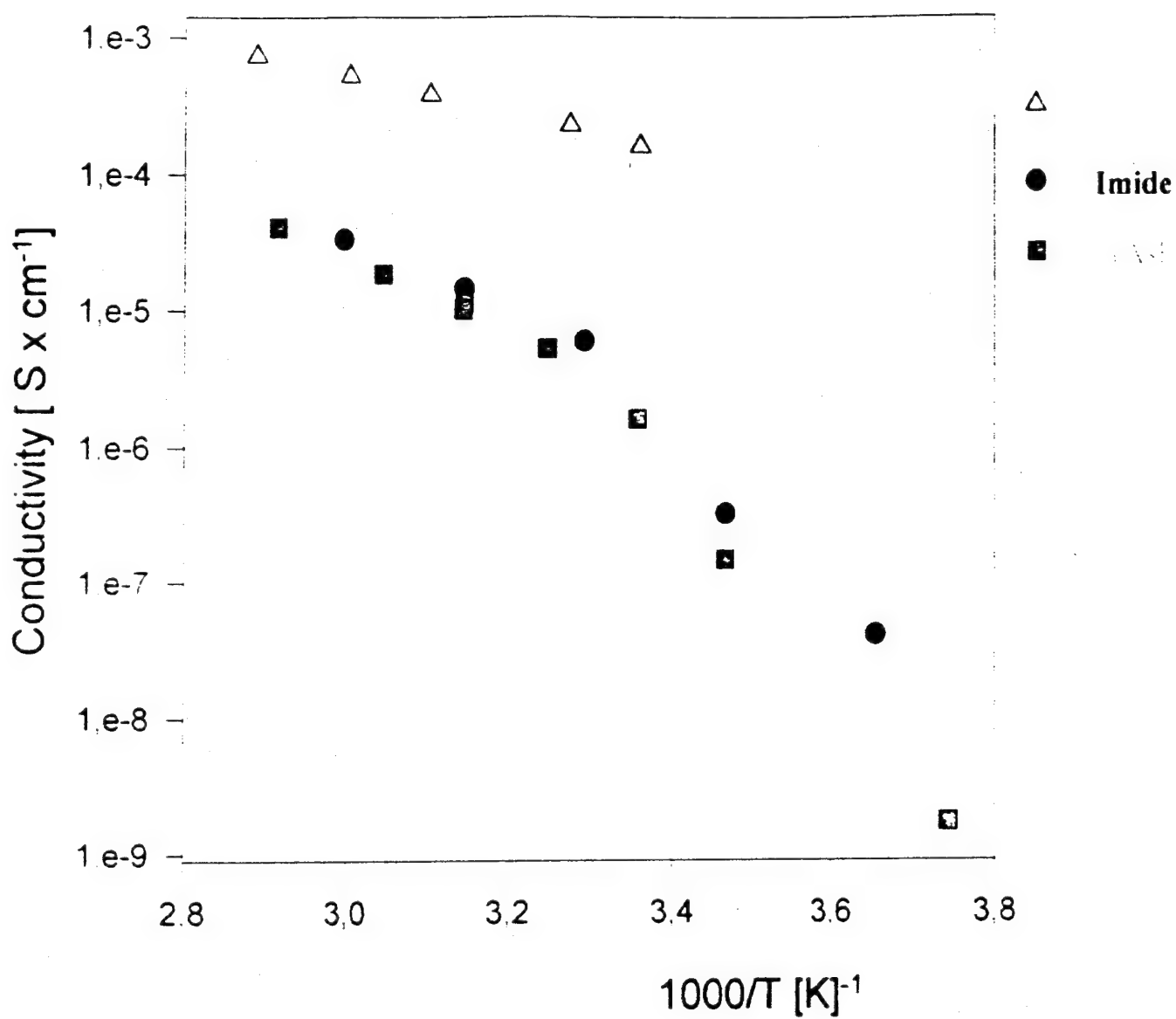
Figure 3. Time dependences of bulk resistance of the polymer electrolyte, the passivating layer resistance and the concentration gradient diffusion resistance.

Figure 4. Lithium-7 NMR absorption spectrum of sample D (Table 1) at -110°C .

Figure 5. Arrhenius plots of central transition ^7Li NMR line width for the PVdF-based electrolytes.

Figure 6. Arrhenius plots of ^7Li spin-lattice relaxation time for the PVdF-based electrolytes.

Arrhenius Plots



5/3/

Li/PVDF1/Li - Cell

Imaginary [Ohm]

6000

Time evolution of the cell impedance

4000

2000

0

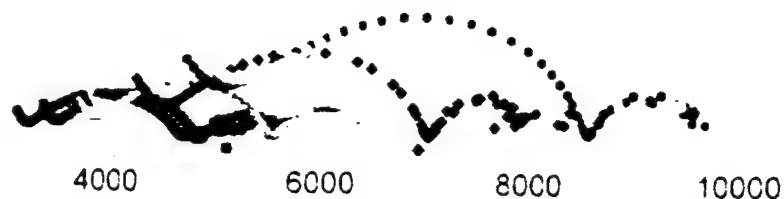
4000

6000

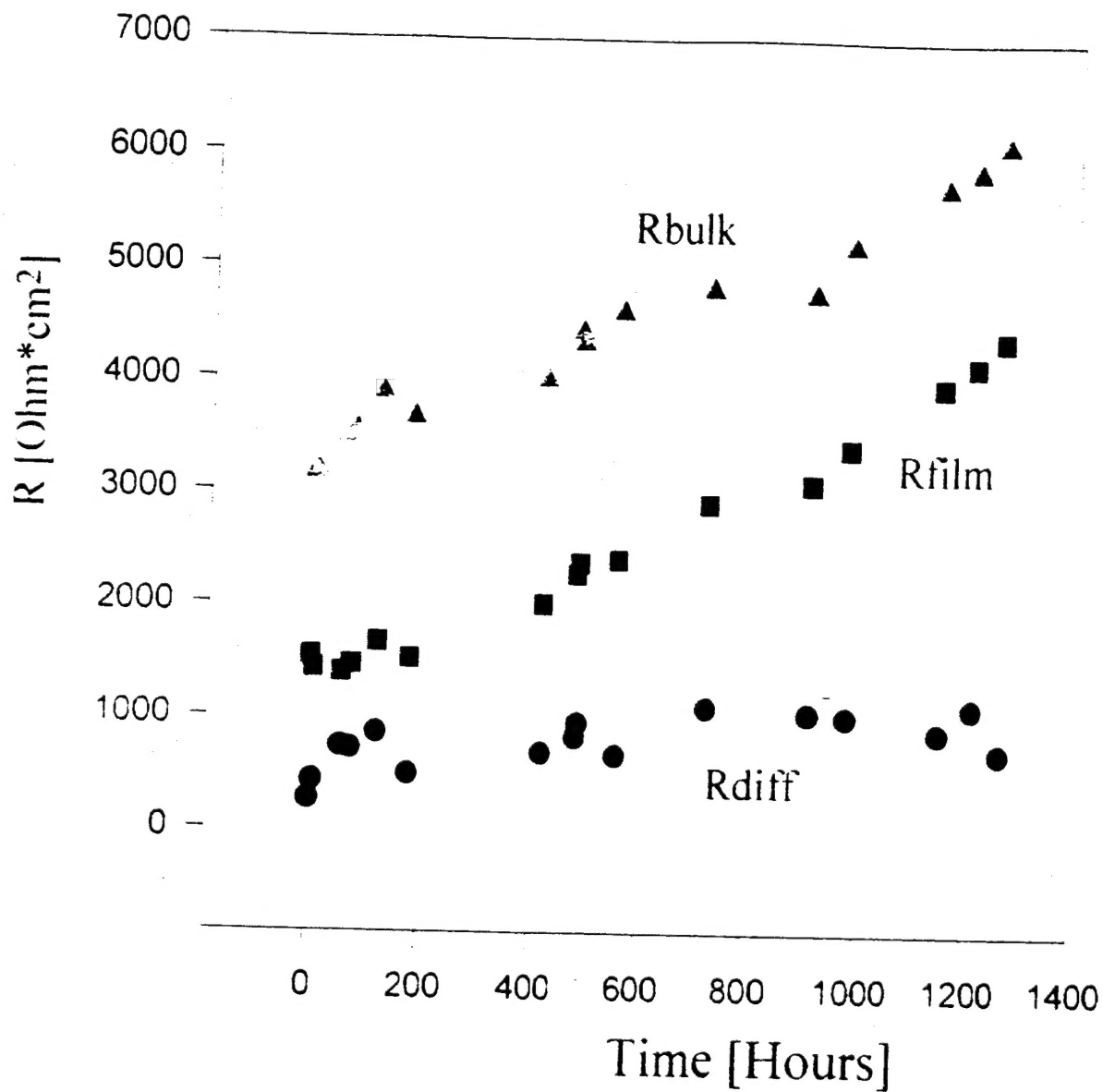
8000

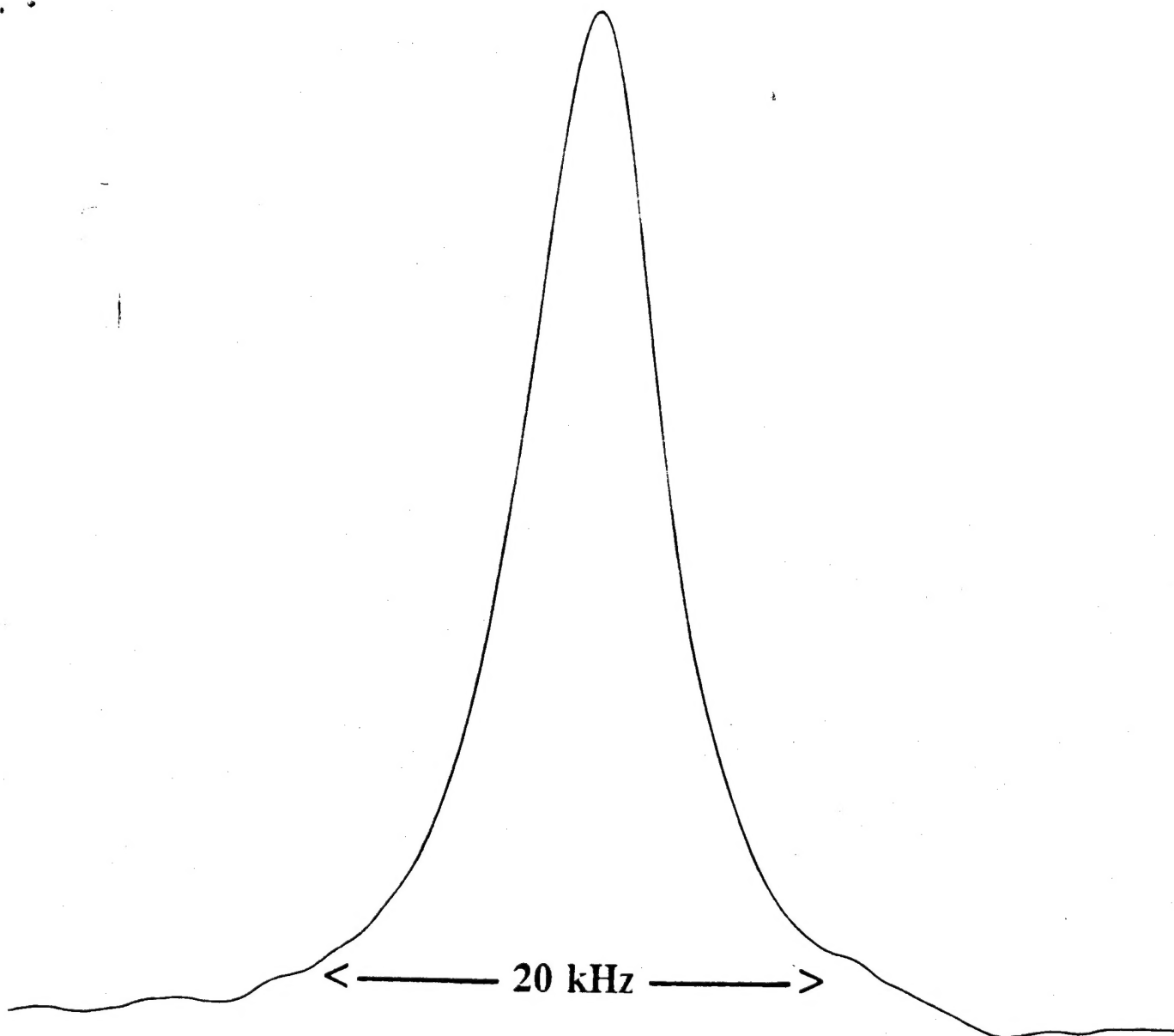
10000

Real [Ohm]



PVDF1 - Li/Interface Stability





F₃₄

